Thermophysical and Magnetic Properties of Two Paramagnetic Liquid Salts: $[C_4\,mim][FeCl_4]$ and $[P_{6,6,6,14}][FeCl_4]$

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The density, heat capacity and viscosity of two magnetic ionic liquids sharing the same Iron(III)-containing anion, specifically, $[C_4mim][FeCl_4]$ and $[P_{6,6,6,14}][FeCl_4]$, have been determined, along with their volumetric expansivity. Their magnetic properties have been studied using SQUID magnetometry. All measurements have been carried out as a function of temperature. The ionic liquids were synthesized using procedures described in the literature [1]. Densities were measured using a commercial Anton Paar DMA 5000 vibrating-tube densimeter in the temperature range 293 < T/K < 363. The accuracy of the data is estimated to be better than $5x10^{-6}$ g/cm^3. The heat capacity measurements were obtained with a differential scanning calorimeter DSC-111, Setaram, France, which was calibrated in enthalpy (Joule effect) and temperature (CRM's, LGC, UK), with an estimated uncertainty of 1.5%. Viscosity data were obtained using an automated microviscometer (Anton Paar AMVn) in the temperature range 278 < *T*/K < 393 and a rheometer (TA AR1500ex), with a specially developed PMMA 40mm diameter cone with an angle of 0:29':38'', to avoid interaction with the magnetic and chemical properties of the samples, for 260 < *T*/K < 370 K. The viscosity data accuracy is estimated to be better than 0.35% for the AMVn viscometer and better than 1.6% for the rheometer.

The atmospheric-pressure isobaric thermal expansion coefficient was calculated from the density data. Isothermal magnetization curves were also obtained, showing that $[C_4mim][FeCl_4]$ and $[P_{6,6,6,14}][FeCl_4]$ are paramagnetic, but while in the first case the magnetic moment value is 5.8 m_B/Fe, close to that of Fe^{3+}, for the latter it is only 4.8 m_B/Fe. The effective concentration of magnetic sites is almost three times greater for $[C_4mim][FeCl_4]$ as compared to $[P_{6,6,6,14}][FeCl_4]$. In this latter case, the experimental isothermal magnetization curves do not follow a Brillouin-type of behavior; alternatively, the results were discussed using the Spin Hamiltonian formalism in terms of both the distortion of the Iron site and covalence effects.

[1] Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G, "Ionic Liquids Based on $FeCl_3$ and $FeCl_2$. Raman Scattering and *ab Initio* Calculations", Inorg. Chem., 40, 2298–2304 (2001)